

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 554 968 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
29.10.1997 Bulletin 1997/44

(51) Int Cl.⁶: **C10G 11/18, C10G 11/02,**
B01J 21/00, B01J 29/00

(21) Application number: **93250038.2**

(22) Date of filing: **01.02.1993**

(54) **Metal passivation/SOx control compositions for FCC**

Metallpassivierung/SOx-Kontrollzusammensetzungen für katalytisches Fluidkracken

Passivation de métaux/compositions de contrôle de SOx pour craquage catalytique à lit fluide

(84) Designated Contracting States:
DE ES FR GB IT NL

(72) Inventor: **Kim, Gwan**
Olney, MD 20832 (US)

(30) Priority: **05.02.1992 US 831610**
09.10.1992 US 959023

(74) Representative: **UEXKÜLL & STOLBERG**
Patentanwälte
Beselerstrasse 4
22607 Hamburg (DE)

(43) Date of publication of application:
11.08.1993 Bulletin 1993/32

(73) Proprietor: **W.R. Grace & Co.-Conn.**
New York, New York 10036 (US)

(56) References cited:
US-A- 4 369 130 **US-A- 4 423 019**
US-A- 4 497 902

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

The present invention relates to compositions which are used to control SO_x emission and the adverse effects of metals such as V and/or Ni encountered in fluid catalytic cracking (FCC) operations, and more particularly to compositions that passivate Ni and/or V during the catalytic cracking of hydrocarbons as well as control SO_x emissions during oxidation regeneration of the catalysts.

Compositions which have been used to passivate Ni and/or V as well as control SO_x emissions typically comprise magnesia, alumina and rare earth oxides.

In particular, U.S. 4,472,267, U.S. 4,495,304 and U.S. 4,495,305 disclose compositions which contain magnesia-alumina spinel supports in combination with rare-earths such as ceria and lanthana, and U.S. 4,836,993 discloses the preparation of magnesium aluminate (MgAl₂O₄) and magnesia-alumina composites that are combined with a rare earth and used as sulfur oxide absorbent in FCC processes. U.S.-A-4 836 993 is silent as to whether or not a spinell phase is formed. None of the examples therein involve compositions containing a combination of MgO, La₂O₃, and Al₂O₃.

While prior compositions have been successfully used to control the adverse effects of V and/or Ni as well as the SO_x emissions from FCC units, the industry requires compositions that are efficient for the passivation of V and/or Ni which is present in hydrocarbon feedstocks.

In addition, V and/or Ni/SO_x control agents which are used in the form of separate particulate additives must have hardness and attrition properties that enable the additive to remain in a circulating FCC catalyst inventory.

It is, therefore, an object of the present invention to provide novel SO_x gettering agent/metals passivation compositions.

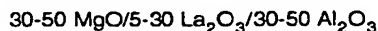
It is another object to provide metal control additives for use in FCC processes that are also efficient for SO_x pick-up and release as well as the passivation of V and/or Ni.

It is a further object to provide magnesia-lanthana-alumina containing metals/SO_x control additives that are resistant to attrition and capable of maintaining sufficiently high surface area when used in the highly abrasive and hydrothermal conditions encountered in a commercial FCC process.

It is yet another object to provide efficient/economical methods for preparing metals/SO_x control additives on a commercial scale.

These and still further objects will become readily apparent to one skilled-in-the-art from the following detailed description, specific examples, and drawing wherein figures 1 and 2 are block diagrams which illustrate preferred methods of preparing the novel compositions of the present invention.

Broadly, the present invention contemplates a novel composition for the passivation of metals and/or the control of SO_x emissions in FCC processes, said composition comprising an oxide base component having the formula:



wherein

- (i) the amounts MgO, La₂O₃ and Al₂O₃ are expressed as wt.% of said component,
- (ii) said MgO is present as a microcrystalline constituent,
- (iii) said oxide base component is virtually MgAl₂O₄ spinel-free, and
- (iv) at least said La₂O₃ and Al₂O₃ are present as a coprecipitate.

The present invention further comprises said novel composition in combination with zeolite containing catalytic cracking compositions which are used to process hydrocarbon feedstocks that contain Ni/V and/or sulfur.

The preferred additive compositions are further characterized by: A fresh surface area of 100 to 300 m²/g following 2-hour air calcination at 538°C, more preferably 130 to 260 m²/g and most preferably 130 to 200 m²/g as determined by the B.E.T. method using nitrogen; a surface area of 100 to 200 m²/g, preferably 100 to 150 m²/g upon 48-hour steaming with 20% steam/80% air at 704°C; a pore volume of 0.4 to 1.0 cm³/g as determined by water; a nitrogen pore volume of at least about 0.3 cm³/g, preferably 0.4 to 0.6 cm³/g from nitrogen porosimetry covering up to 600 Å (60.0 nm) pore diameter at 0.967 relative pressure; an attrition resistance of 0 to 45 Davison Index (DI) as determined by the method disclosed in U.S. 3,650,988 and 4,247,420 for fresh material after 2-hour air calcination at 538°C; a microcrystalline MgO component before and after steaming as determined by X-ray diffraction. When used as an SO_x control additive, the composition preferably includes a total promoter metal content of 1 to 15 weight percent as oxides. The promoter metal(s) is preferably selected from the group consisting of Ce, Pr, Ti, Nb, V and mixtures thereof. The promoter preferably consists of 2 to 10% by weight ceria and/or vanadia; a sodium content of less than about 1% by weight Na₂O, and preferably less than 0.5% by weight Na₂O; and a bimodal distribution of mesopores in the 40-200 Å (4.0-20.0 nm) and 200-2000 Å (20.0-200.0 nm) regions. The median (pore volume basis) pore diameter from nitrogen

porosimetry ranges from approximately 50 Å (5 nm) to 100 Å (10 nm), depending on the final calcination condition, e.g., simple air calcination at 538°C or air calcination at 704°C with varying levels of steam.

Referring to Figure 1, it is seen that the composition may be prepared by a multi-step process described as follows:

- (1) A solution containing a lanthanum salt such as lanthanum nitrate is reacted with a solution of sodium aluminate under conditions wherein a separate stream of lanthanum nitrate is combined with a stream of sodium aluminate solution over a period of 20 to 60 minutes in a stirred reaction vessel to form a lanthanum-aluminum hydrous oxide coprecipitate.
- (2) The coprecipitated lanthanum-aluminum hydrous oxide slurry mixture of step (1) is aged at a pH of 9.3 to 9.7 for a period of 0.1 to 2 hours at a temperature of 20 to 65°C.
- (3) The aged slurry of step (2) is then reacted with an aqueous solution of magnesium nitrate and a solution of sodium hydroxide which are added as separate streams over a period of 20 to 60 minutes to a stirred reaction vessel at a pH of about 9.5 and at a temperature of 20 to 65°C to obtain a ternary magnesium/lanthanum/aluminum hydrous oxide precipitate.
- (4) The ternary oxide precipitate of step (3) is separated by filtration, washed with water to remove extraneous salts, preferably spray dried, and calcined at a temperature of 450 to 732°C to obtain a ternary oxide base composition that is free of MgAl_2O_4 spinel and having a surface area of 130 to 260 m^2/g .
- (5) The ternary oxide base obtained in step (4), when used as an SOx additive, is preferably impregnated with solutions of cerium and/or vanadium and optionally titanium to impart a ceria content of about 5 to 15 weight percent and a vanadia content of about 1 to 10 weight percent and optionally a titania content of 0 to 10 weight percent.
- (6) The impregnated base of step (5) is then dried and calcined at a temperature of 450 to 700°C.

Alternative methods for preparing the novel compositions are outlined in Figure 2 wherein: the magnesium/lanthanum/rare earth nitrate, sodium hydroxide, sodium aluminate solutions described above are combined in a mixer (typically a four-port mix-pump) to form a Mg-La/RE-Al ternary hydrous oxide coprecipitate which is aged for about 10 to 60 minutes and then further processed into particulate SOx control additives as shown in alternative processing methods (A) and (B).

The preferred compositions of the present invention are prepared in the form of microspheres which have a particle size range of 20 to 200 μm and a Davison attrition index (DI) of 0 to 45, preferably 0 to 15, and are suitable for use as SOx control additive in FCC processes.

The metals control additive composition may be combined with conventional commercially available FCC catalyst zeolite-containing FCC catalysts which typically contain 10 to 60 weight percent zeolite such as Type Y, ultrastable Y, ZSM-5 and/or Beta zeolite dispersed in an inorganic oxide matrix, such as the Octacat®, XP®, Super-D®, and DA® grades produced and sold by the Davison Chemical Division of W. R. Grace & Co.-Conn.

It is contemplated that the metals control SOx control additive compositions may also be incorporated in FCC catalyst particles during manufacture in a catalyst preparation procedure such as disclosed in U.S. 3,957,689, U.S. 4,499,197, U.S. 4,542,118 and U.S. 4,458,623 and Canadian 967,136.

The metals control additive compositions (unpromoted) are typically added to a FCC catalyst in amounts ranging from 0.2 to 15 weight percent and more preferably 0.5 to 5 weight percent. In addition, the catalyst composition may include about 1 to 15 weight percent of the ceria/vanadia promoted compositions for control of SOx emissions. The promoted/unpromoted compositions may be pre-blended prior to adding to a FCC unit. In one preferred embodiment, the FCC catalyst will also contain a noble metal combustion/oxidation catalyst such as Pt and/or Pd in amounts of 0.1 to 10 ppm. The FCC catalyst/SOx control composition mixture is reacted with hydrocarbon gas-oil and residual feedstocks that contain as much as 2.5 weight percent sulfur (S), 0.005 weight percent Ni and/or 0.005 weight percent V, at temperatures of 520 to 1100°C (cracking reaction) and 700 to 750°C (regeneration). In typical commercial FCC operations it is anticipated that the FCC catalyst may accommodate up to about one weight percent Ni and/or V and still contain an acceptable level of activity and/or selectivity.

Cracking activity is determined by the so-called microactivity test (MAT) method according to ASTM #D 3907-8.

The Davison Index (DI) is determined as follows:

A sample of catalyst is analyzed to determine the weight of particles in the 0 to 20 and 20+ μm size ranges. The sample is then subjected to a 1 hour test in a fluid catalyst attrition apparatus using a hardened steel jet cup having a precision bored orifice. An air flow of 21 liters a minute is used. The Davison Index is calculated as follows:

$$\text{Davison Index} = \frac{\text{wt. \% 0-20 } \mu\text{m material formed during test}}{\text{wt. original 20+ } \mu\text{m fraction}}$$

Having described the basic aspects of the present invention, the following examples are included to illustrate specific embodiments.

Example 1

A coprecipitation run was carried out by feeding one acidic stream and one basic stream simultaneously into a high speed mix-pump reactor with multiports, allowing the viscous product stream to fall into 4000 g of heel water in a kettle maintained at 38-40°C with good agitation. The acidic feedstream contained 654.4 g of MgO and 413.3 g of La-rich rare earth oxide, all in the form of nitrate in a total volume of 9840 ml. The basic feedstream had a sodium aluminate solution bearing 654.4 g of Al_2O_3 along with 320 g of 50 weight percent sodium hydroxide solution in a total volume of 9840 ml. While these two streams were fed at an equal rate of 400 ml/minute, the feed rate of stream No. 3 with 16 weight percent sodium hydroxide solution was adjusted so as to control pH of the slurry in the kettle at 9.4 - 9.5. After aging the slurry under this condition for 15 minutes and confirming pH was at 9.5 at the end of aging, the slurry was immediately vacuum filtered. The filtercake was then homogenized using a high-shear mixer, Drais milled once, rehomogenized, and was spray dried.

A 400 g portion of the above resulting microspheres was slurried once in 1000 g of tap water at room temperature for 3 minutes, and then was washed once with another 1000 g of room-temperature tap water, and filtered. After overnight drying in a 115°C oven, the material was air calcined at 704°C for 2 hours. Properties of the resulting material, hereafter to be referred to as 1A, are as follows: Chemical composition (weight percent): 36.8% MgO, 20.8% La_2O_3 , 0.1% CeO_2 , 23.4% total rare earth oxide, 0.2% Na_2O , and 39.1% Al_2O_3 . The results from X-ray powder diffraction scan showed that this material was virtually MgAl_2O_4 spinel-free before and after 5-hour exposure to flowing (1.5 liters/minute) air containing 20 volume % steam at 788°C. Average particle size: 99 μm , attrition resistance: 17 DI (Davison Index), BET (N_2) surface area: 181 m^2/g .

A set of four 60-gram samples was prepared by physically blending an ORION® family of Davison FCC catalyst with 0, 5, 10, and 15 weight percent (on a dry basis) of 1A. Each sample was then treated according to the following protocol: Heated to 204°C and allowed one-hour soak at this temperature in a muffle furnace; Raised at a rate of approximately 4°C/minute to 677°C and then allowed to soak at this temperature for 3 hours; Cooled to room temperature; Impregnated with vanadium naphthenate in pentane to completely and uniformly cover all particles with vanadium; Allowed pentane to evaporate away in a muffle furnace at room temperature; Heated to 204°C and held for one hour; Charged into an Inconel fluid-bed reactor; Steamed for 5 hours in this fluidized bed at 788°C, with 80 vol.% steam (6.8 g $\text{H}_2\text{O}/\text{hour}$) and 20% vol.% air. Each sample was then examined for chemical and physical properties, especially the zeolite surface area. The results are presented in Table I. The data reveal unequivocally that the material 1A is highly effective in protecting zeolites in the FCC catalyst from vanadium attack. With only 5 weight percent of 1A in the blend, the zeolites in this blend retained approximately 93% more zeolite area than without 1A. With 10 weight percent of 1A, there is a 122% increase in zeolite area as a result of preferential vanadium capture by the material of this invention, 1A.

Example 2

Another additive having a composition slightly different from 1A of Example 1 was prepared in exactly the same manner as in Example 1, except for the feedstream composition. The acidic feedstream consisted of 9840 ml of solution containing 671.6 g of MgO, 275.5 g of La-rich rare earth oxide, and 123.1 g of CeO_2 , all in the form of nitrate. The basic feedstream contained 671.6 g of Al_2O_3 in the form of sodium aluminate solution along with 320 g of 50 weight percent sodium hydroxide solution in a total volume of 9840 ml.

The material obtained from spray drying, slurring, washing, drying, and 2 hour air calcination at 704°C, hereafter to be referred to as 2A, had the following properties: Chemical composition (weight percent): 38.0% MgO, 13.8% La_2O_3 , 5.7% CeO_2 , 21.1% total rare earth oxide, 0.4% Na_2O , 0.3% SO_4 , and 39.8% Al_2O_3 . This material, 2A, also showed virtually no MgAl_2O_4 spinel before and after 5-hour steaming (80% steam/20% air) described in Example 1.

In exactly the same manner as in Example 1, another set of four 60-gram samples, ORION/2A blend, was prepared, and was treated with the same vanadium impregnation and steaming as described in Example 1. The results on this set of blends are presented in Table II. The data essentially confirm what has already been observed in Example 1.

Example 3

A 71.82 g (70.00 g on a dry basis) portion of 2A of Example 2 was sprayed with fine mist of ammoniacal vanadium tartrate solution bearing 1.80 g of V_2O_5 to incipient wetness using an atomizer and a rotary mixer. After allowing the impregnated material to stand at room temperature for approximately 30 minutes, the material was oven dried overnight at 115°C, and then was air calcined at 538°C for one hour. The resulting material, hereafter to be referred to as 3A, was virtually MgAl_2O_4 spinel-free according to X-ray powder diffraction scan before and after 48-hour exposure to flowing air (1.5 liters/minute) containing 20 vol.% steam at 702°C. The properties of this material are as follows: Chemical composition (weight percent): 35.9% MgO, 13.5% La_2O_3 , 5.6% CeO_2 , 20.8% total rare earth oxide, 0.4% Na_2O ,

2.7% V_2O_5 , and 39.4% Al_2O_3 . Average particle size: 54 μm , Attrition resistance: 8 DI. BET (N_2) surface areas before and after 48-hour steaming (20% steam/80% air) were 181 and 124 m^2/g , respectively.

The above resulting material, 3A, was evaluated on the bench as a potential SOx additive, i.e., SOx transfer catalyst, capturing SO_3 in the oxidizing environment of the regenerator and releasing sulfur in the form of H_2S in the reducing environment of the riser. Since the performance of SOx additive can be assessed largely by the capacity of SO_3 capture and the release capability in the form of H_2S , the following two tests were carried out for this sample:

(1) Capacity for SO_3 capture: A blend was prepared from 9.950 g of steamed (6 hours in a fluidized bed at 760°C and 34.47 kPag (5 psig)) OCTACAT® (another Davison FCC catalyst) and 0.050 g of fresh 3A, all on a dry basis. It was charged into an Inconel reactor having an I.D. of 1.04 cm, and was subjected to two-stage treatments: First, a 30-minute reduction in flowing (1.5 liters total/min.) N_2 containing 2 vol.% H_2 , and next, a 30-minute oxidation in flowing (1.5 liters total/min.) N_2 containing 4 vol.% O_2 and 0.0900 vol.% SO_2 at 732°C. After each treatment, the sample was discharged, homogenized, and the sulfate level was determined on a one-gram portion removed from the sample. The weight percent SO_4 found in this sample as a result of the oxidation treatment was 0.46%. This was taken as a measure of the capacity for SO_3 capture. The capacity found for this sample represents approximately 85% of the theoretical maximum - the maximum weight percent SO_4 that can be accumulated in this sample is approximately 0.54% when all metals but aluminum form stoichiometric sulfates at 732°C. The material of this invention, 3A, thus has a quite high capacity for SO_3 storage.

(2) Release capability: A 0.40 g sample of fresh 3A was placed in a down-flow Vycor glass reactor, and was exposed to flowing N_2 containing 9.50 vol.% O_2 and 0.6000 vol.% SO_2 at a total flow rate of 126 ml/minute and 732°C for a period of 3 hours, and cooled in flowing N_2 for discharge. A 0.10 g portion of the above-treated sample was examined by temperature-programmed reduction (TPR)/mass-spectrometer in a ramp-mode at a rate of 20°C/min., using propane at 14.2 ml/min. as a reducing agent. During the course of this TPR run, the concentration of H_2S was determined as a function of temperature by monitoring mass number 34. The TPR scan data plot, H_2S counts vs. temperature for this sample showed an onset temperature - the temperature here represents a sort of dynamic temperature rather than equilibrium or steady/isothermal temperature - of approximately 500°C, which is well below the riser bottom temperature. Thus, 3A is expected to show a release capability.

Example 4

Three of the four steamed samples with vanadium listed in Table I for Example 1 were evaluated by microactivity test (MAT) using a fixed bed reactor described in ASTM Method No. D3907. The feedstock employed in MAT evaluation was a sour, imported heavy gas oil with properties shown in Table III. The MAT data at constant conversion summarized in Table IV clearly demonstrate what one can expect from the materials of this invention. Namely, there is activity benefit, as reflected in the substantially decreased catalyst-to-oil weight ratio (C/O) for the FCC catalyst samples blended with some of the materials of this invention. There are also selectivity benefits - especially noticeable are the drastically lowered coke and H_2 gas yields and substantially increased gasoline yield.

Example 5

An additive with a composition very slightly different from 2A was prepared in exactly the same manner as in Example 2 by making minor changes in Mg/rare earth/Al ratio for the feedstreams. The material obtained from spray drying, followed by slurring, washing, drying, and 2-hour calcination at 538°C, hereafter to be referred to as 5A, had the following properties: Chemical composition (weight percent): 39.1% MgO , 12.0% La_2O_3 , 7.4% CeO_2 , 20.7% total rare earth oxide, 0.1% Na_2O , 0.3% SO_4 , and 39.6% Al_2O_3 . Some of the physical properties are - 0.67 g/cm^3 average bulk density, 73 μm average particle size, 187 m^2/BET (N_2) surface area, 0.485 N_2 pore volume, 66 Å (6.6 nm) median (N_2 -PV) pore diameter, and 10 DI.

A set of three 60-gram samples of ORION®/5A blend was prepared, and was steamed with vanadium in exactly the same manner as in Example 1. Properties and MAT data at constant conversion for these samples are presented in Tables V and VI, respectively. These data essentially confirm the kind of results we have already shown in Tables I and IV for the materials of this invention.

TABLE I

Effect of Additive 1A on FCC Catalyst				
Blend (Wt.) Ratio 1A/FCC Cat.	0/100	5/95	10/90	15/85
Chemical Composition (wt.%) after steaming with vanadium				
Al ₂ O ₃	32.63	33.02	33.35	33.44
Na ₂ O	0.43	0.42	0.42	0.39
SO ₄	0.51	1.11	1.27	1.07
MgO	0.08	2.38	3.98	6.00
RE ₂ O ₃	1.51	2.79	3.76	5.02
Ni	0.003	0.002	0.003	0.002
V	0.522	0.568	0.550	0.560
Properties after steaming with vanadium				
Unit Cell, Å*	24.23	24.23	24.24	24.23
Pk. Ht.	12	19	25	24
Total S.A., m ² /g	68	114	127	129
Zeolite S.A., m ² /g	45	83	90	89

* 1Å = 0.1 nm

TABLE II

Effect of Additive 2A on FCC Catalyst				
Blend (Wt.) Ratio 2A/FCC Cat.	0/100	5/95	10/90	15/85
Chemical Composition (wt.%) after steaming with vanadium				
Al ₂ O ₃	32.52	32.82	32.67	34.26
Na ₂ O	0.44	0.43	0.42	0.43
SO ₄	0.49	1.08	1.07	1.01
MgO	0.08	2.30	4.18	5.77
RE ₂ O ₃	1.51	2.60	3.57	4.53
Ni	0.002	0.003	0.003	0.003
V	0.495	0.548	0.542	0.537
Properties after steaming with vanadium				
Unit Cell, Å*	24.23	24.24	24.26	24.24
Pk. Ht.	19	30	34	36
Total S.A., m ² /g	81	127	143	149
Zeolite S.A., m ² /g	53	87	99	102

* 1Å = 0.1 nm

Table III

Properties of Sour, Imported, Heavy Gas Oil (SIHGO)	
API gravity at 16°C	22.5
Sulfur (wt.%)	2.6
Nitrogen (wt.%)	0.086
Conradson Carbon (wt.%)	0.25
Aniline Point (°C)	73
K Factor	11.6
D-1160 (°C)	
IBP	217

EP 0 554 968 B1

Table III (continued)

Properties of Sour, Imported, Heavy Gas Oil (SIHGO)	
5	307
10	324
20	343
40	382
60	423
80	472
90	500
95	524

TABLE IV

Interpolated, Mass-Balanced MAT Yields at 55 wt.% Conversion Samples: 5h/788°C Steamed (80% steam/
20% air at 0 kPag (0 psig)) 1A/ORION® Blends with 5000 ppm V

Test Conditions: 527°C, 30 sec. Contact Time, SIHGO Feed

Blend wt. Ratio 1A/FCC Cat.	0/100	5/95	10/90
Cat./Oil Weight Ratio	5.5	3.5	3.1
MAT Yields @ 55% Conversion			
H ₂	0.95	0.52	0.36
C ₁ + C ₂ 's	2.3	1.8	1.6
C ₃ =	2.8	3.0	3.1
Total C ₃ 's	3.4	3.5	3.6
C ₄ =	3.8	4.0	4.1
iso C ₄	1.2	1.6	1.8
Total C ₄ 's	5.5	6.1	6.4
C ₅ + Gasoline	36.1	38.6	39.4
LCO	26.6	26.4	26.0
640 + Bottoms	18.4	18.6	19.0
Coke	6.7	4.4	3.5
GC-RON	92.6	91.6	91.0
GC-MON	81.3	80.5	80.3
n-Paraffins	4.5	4.7	4.5
Iso-Paraffins	24.1	26.7	28.5
Olefins	26.5	25.5	25.3
Aromatics	36.2	33.8	31.9
Napthenes	8.5	9.4	9.9

TABLE V

Effect of Additive 5A on FCC Catalyst

Blend (Wt.) Ratio 5A/FCC Cat.	0/100	5/95	10/90
Chemical Composition (wt.%) after steaming with vanadium			
Al ₂ O ₃	32.28	32.86	32.26

TABLE V (continued)

Effect of Additive 5A on FCC Catalyst			
Blend (Wt.) Ratio 5A/FCC Cat.	0/100	5/95	10/90
Chemical Composition (wt.%) after steaming with vanadium			
Na ₂ O	0.43	0.42	0.39
SO ₄	0.50	1.07	1.08
MgO	0.11	2.25	4.31
RE ₂ O ₃	1.53	2.60	3.66
Ni	0.002	0.003	0.002
V	0.511	0.525	0.537
Properties after steaming with vanadium			
Unit Cell, Å*	24.26	24.24	24.25
Pk. Ht.	21	32	35
SA (Z/M), m ² /g	62/29	88/36	96/42

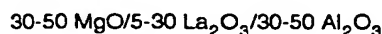
* 1Å = 0.1 nm

TABLE VI

Interpolated, Mass-Balanced MAT Yields at 60 wt.% Conversion Samples: 5h/788°C Steamed (80% steam/ 20% air at 0 kPag (0 psig)) 5A/FCC Catalyst Blends with 5000 ppm V			
Test Conditions: 527°C, 30 sec. Contact Time, SIHGO Feed			
Blend wt. Ratio 5A/FCC Cat.	0/100	5/95	10/90
Cat./Oil Weight Ratio	5.4	4.3	3.6
H ₂	0.98	0.73	0.46
C ₁ + C ₂ 's	2.4	2.1	1.9
C ₃ =	3.2	3.3	3.4
Total C ₃ 's	3.8	4.0	4.1
C ₄ =	4.2	4.3	4.4
Iso C ₄	1.5	1.8	2.1
Total C ₄ 's	6.2	6.6	7.0
C ₅ + Gasoline	39.6	40.8	41.6
LCO	25.1	24.7	24.5
640 + Bottoms	14.9	15.3	15.5
Coke	7.1	5.8	4.8
GC-RON	92.1	91.4	90.9
GC-MON	81.2	80.9	80.6
n-Paraffins	4.6	4.9	4.5
Iso-Paraffins	27.5	29.5	31.1
Olefins	22.5	21.6	21.2
Aromatics	37.7	36.2	34.5
Naphthenes	7.7	8.3	9.0

Claims

1. A composition for the passivation of metals and/or the control of SO_x emissions in FCC processes, said composition comprising an oxide base component having the formula:



wherein

- (i) the amounts MgO, La₂O₃ and Al₂O₃ are expressed as wt.% of said component,
- (ii) said MgO is present as a microcrystalline constituent,
- (iii) said oxide base component is virtually MgAl₂O₄ spinel-free, and
- (iv) at least said La₂O₃ and Al₂O₃ are present as a coprecipitate.

2. A composition for the control of SO_x emissions in FCC processes according to claim 1 wherein said composition further comprises, based on the overall composition, 1-15 wt.% of promoters for SO₂ oxidation and/or H₂S release selected from the oxides of Ce, Pr, Ti, Nb, V and mixtures thereof.

3. The composition according to claims 1 or 2 wherein the entire oxide base component is a coprecipitate.

4. The composition according to any of claims 1-3 wherein said composition has a surface area of 100-300 m²/g.

5. The composition according to claim 4 wherein said composition has a surface area of 100-200 m²/g after heating to 704°C for 48 hours in the presence of 20% steam and 80% air.

6. An FCC catalyst composition comprising (a) a zeolite-containing component for cracking hydrocarbons, and (b) the composition according to claims 1 to 5.

7. The composition of claim 6 where said zeolite-containing component comprises a zeolite selected from the group consisting of type Y, ultrastable Y, ZSM-5, Beta and mixtures thereof dispersed in an inorganic oxide matrix.

8. A method of cracking hydrocarbon feedstocks comprising contacting said feedstock with an FCC catalyst composition according to claims 6 or 7 at elevated temperature whereby catalytic cracking of said hydrocarbons occurs.

9. The method according to claim 8 wherein said feedstock contains V and/or Ni.

10. The method according to claim 9 wherein said feedstock contains sulfur and said FCC catalyst composition contains a composition for control of SO_x emissions according to claim 2.

Patentansprüche

1. Zusammensetzung zur Passivierung von Metallen und/oder zur Kontrolle von SO_x-Emissionen in katalytischen Fluidcrackverfahren, die eine Oxid-Basiskomponente mit der Formel:



umfaßt, wobei

- (i) die Mengen an MgO, La₂O₃ und Al₂O₃ als Gew.% der Komponente angegeben sind,
- (ii) das MgO als ein mikrokristalliner Bestandteil vorhanden ist,
- (iii) die Oxid-Basiskomponente nahezu MgAl₂O₄-spinnelfrei ist und
- (iv) mindestens La₂O₃ und Al₂O₃ als eine Mitfällung vorhanden sind.

2. Zusammensetzung zur Kontrolle von SO_x-Emissionen in katalytischen Fluidcrackverfahren nach Anspruch 1, die auf Basis der Gesamtzusammensetzung weiterhin 1-15 Gew.% Beschleunigungsmittel für die SO₂-Oxidation und/

oder die H₂S-Freisetzung umfaßt, die aus den Oxiden von Ce, Pr, Ti, Nb, V sowie deren Mischungen ausgewählt sind.

3. Zusammensetzung nach Ansprüchen 1 oder 2, worin die gesamte Oxid-Basiskomponente eine Mitfällung ist.
4. Zusammensetzung nach einem der Ansprüche 1-3, die eine Oberfläche von 100-300 m²/g aufweist.
5. Zusammensetzung nach Anspruch 4, die nach 48stündiger Erwärmung auf 704°C in Gegenwart von 20% Dampf und 80% Luft eine Oberfläche von 100-200 m²/g aufweist.
6. Eine Katalysatorzusammensetzung für katalytische Fluidcrackverfahren, die (a) eine Zeolith-enthaltende Komponente zum Cracken von Kohlenwasserstoffen und (b) die Zusammensetzung gemäß den Ansprüchen 1 bis 5 umfaßt.
7. Zusammensetzung nach Anspruch 6, in der die Zeolith-enthaltende Komponente ein Zeolith umfaßt, das aus der Gruppe, bestehend aus Typ Y, ultrastabilem Y, ZSM-5, Beta und Mischungen davon, ausgewählt und in einer Matrix eines anorganischen Oxids dispergiert ist.
8. Verfahren zum Cracken von Kohlenwasserstoff-Einsatzmaterial, bei dem das Einsatzmaterial bei erhöhter Temperatur mit einer Katalysatorzusammensetzung für katalytische Fluidcrackverfahren gemäß den Ansprüchen 6 oder 7 kontaktiert wird, wodurch die Kohlenwasserstoffe katalytisch gecrackt werden.
9. Verfahren nach Anspruch 8, bei dem das Einsatzmaterial V und/oder Ni enthält.
10. Verfahren nach Anspruch 9, bei dem das Einsatzmaterial Schwefel enthält und die Katalysatorzusammensetzung für katalytische Fluidcrackverfahren eine Zusammensetzung zur Kontrolle von SO_x-Emissionen gemäß Anspruch 2 enthält.

Revendications

1. Composition pour la passivation des métaux et/ou le contrôle des émissions de SO_x dans des procédés de FCC, ladite composition comprenant un composant de base d'oxyde ayant la formule :



où

- (i) les quantités MgO, La₂O₃ et Al₂O₃ s'expriment en % en poids dudit composant,
- (ii) ledit MgO est présent en tant que constituant microcristallin
- (iii) ledit composant de base d'oxyde est virtuellement MgAl₂O₄ sans spinelle, et
- (iv) au moins ledit La₂O₃ et ledit Al₂O₃ sont présents en tant que coprécipité.
2. Composition pour le contrôle des émissions de SO_x dans des procédés de FCC selon la revendication 1, où ladite composition comprend de plus, en se basant sur la composition totale, 1-15 % en poids de promoteurs pour l'oxydation de SO₂ et/ou la libération de H₂S sélectionnés parmi les oxydes de Ce, Pr, Ti, Nb, V et leurs mélanges.
3. Composition selon la revendication 1 ou 2 où tout le composant de base d'oxyde est un coprécipité.
4. Composition selon l'une quelconque des revendications 1-3 où ladite composition a une aire superficielle de 100-300 m²/g.
5. Composition selon la revendication 4 où ladite composition a une aire superficielle de 100-200 m²/g après chauffage à 704°C pendant 48 heures en présence de 20 % de vapeur et 80 % d'air.
6. Composition d'un catalyseur de FCC comprenant (a) un composant contenant de la zéolite pour le craquage des hydrocarbures et (b) la composition selon les revendications 1 à 5.

7. Composition de la revendication 6 où ledit composant comprenant de la zéolite comprend une zéolite sélectionnée dans le groupe consistant en Y, Y ultrastable, ZSM-5, Bêta et leurs mélanges en dispersion dans une matrice d'oxyde inorganique.

5 8. Méthode de craquage des charges d'alimentation d'hydrocarbures consistant à mettre ladite charge d'alimentation en contact avec une composition un catalyseur de FCC selon les revendications 6 ou 7 à température élevée pour qu'ainsi se produise un craquage catalytique desdits hydrocarbures.

10 9. Méthode selon la revendication 8 où ladite charge d'alimentation contient V et/ou Ni.

10. Méthode selon la revendication 9 où ladite charge d'alimentation contient du soufre et ladite composition du catalyseur de FCC contient une composition pour le contrôle des émissions de SO_x selon la revendication 2.

15

20

25

30

35

40

45

50

55

FIGURE I

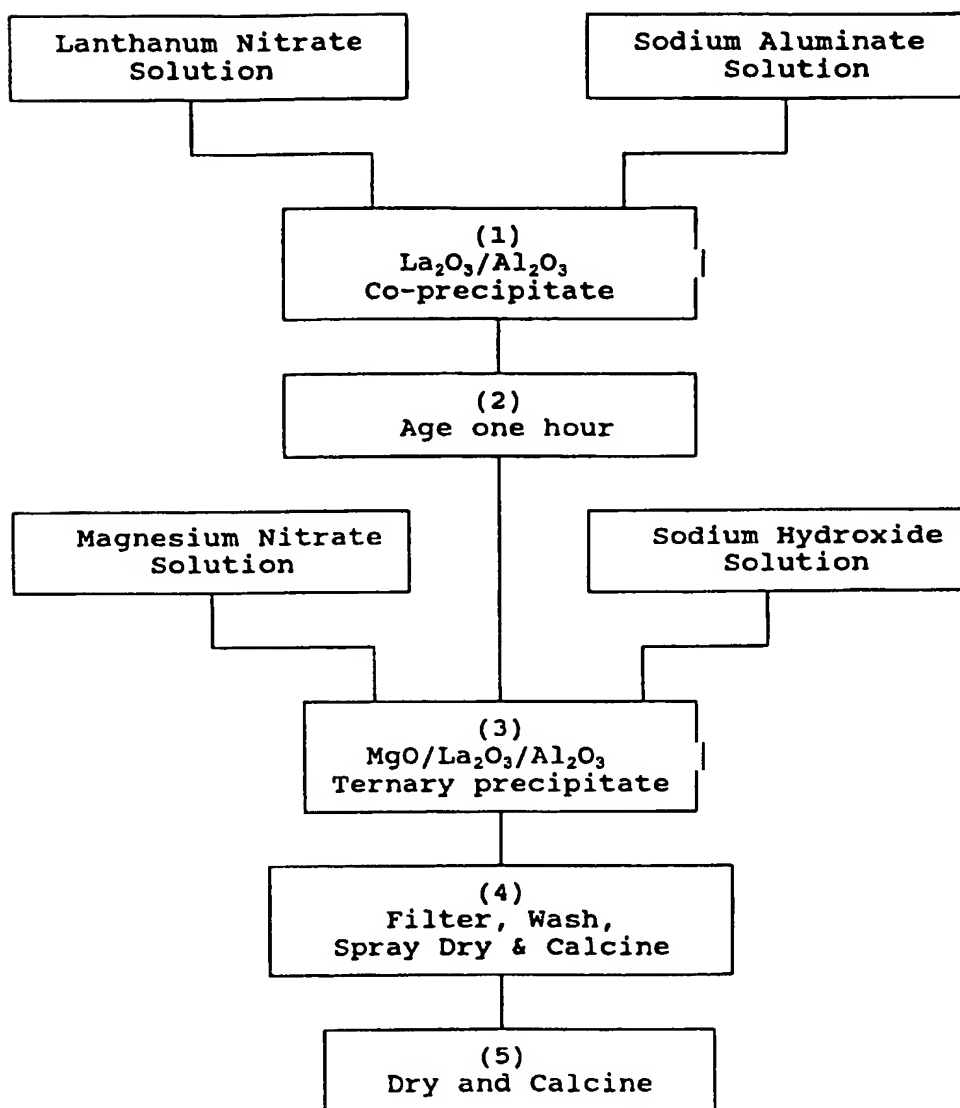


FIGURE II

